Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 14 (2012) 418 – 423

Energy Procedia

3D Simulations of electric field on 40 kA sodium electrolysis cell

LIU Zhongxing[a], WANG Liangliang[a], WU Yongfu[a], WANG Xiaoqing[b,a]*

[a]*Inner Mongolia University of science And technology ,Bao tou,014010,China*
[b]*Baotou Research Institute of Rare Earths,Bao tou,014010,China*

Abstract

Three-dimensional mathematical model for one quarter groove of 40KA sodium cell was established, based on the feature of its structure. The electric field with apertures drilled at different electrodes, where the slot voltages was analyzed and discussed, was simulated utilizing the features of Finite Element Software ANSYS with multiple attributes. The result provides the theoretical basis for the process optimization and the design of electrolyzer.

Key word: electrobath; electric field; numerical simulation;

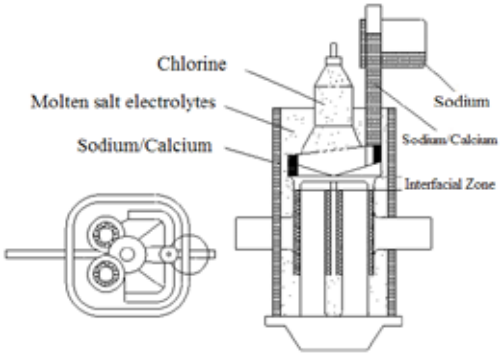
1. Introduction

For the electrolysis cell research, the basic work is to study the power balance, material balance and heat balance in the cell. The solutions to these three balance-problems are to study the physical field of the cell. There are many complex physical fields in the cell. In these fields, electric field is the basis of other physical fields. The electric field of the conductor inside the sodium cell was studied to master the electric field distribution of the anode; cathode and electrolyte melt, and also provide a theoretical basis to the cell's stability and efficient production. Literature [1, 2] had simulated the electric field of two-dimension openings and three-dimensional polar distance change, and these can not analyze the electric field results well. In this paper, finite element analysis software ANSYS is used to simulate the three-dimensional electric field of 40KA sodium cell [3], and analyze the electric field in the case of different openings of cell's electrode. As was known to us, this paper provides a theoretical basis to the development and structure optimization of the sodium cell.

* LIU Zhongxing. Tel.: 04725951612 *E-mail address*: liuzx@imust.cn
National Natural Science Foundation of China（51064020）.Natural Science Foundation of Inner Mongolia （2011MS0703）

doi:10.1016/j.egypro.2011.12.952

As shown in Fig.1, Electrolysis of sodium was carried out in the four anode East Sri Lanka electrolysis cell. Electrolyte was ternary molten salt system which was composed of NaCl (30%)-CaCl2 (20%)-BaCl2 (50%) [4]. A certain electrolytic temperature was kept entirely by the direct current energy



（a）—Vertical view （b）—Front view

Fig. 1. Four anode East Sri Lanka electrolysis cell

2. Materials and methods

2.1 Simplified physical model of sodium cell

Because of many practical constraints, this paper had to do some simplification and approximation：

- Without considering the other cell ancillary equipments (e.g.: wire gauze, gas-collecting device) on the impact of the electric field；
- Without considering the groove chamfer on the impact of the electric field；
- There isn't any leakage of electrical energy and all current move through the anode and cathode. The total number of the current is 40000A that is evenly distributed in four anode and each anode's current is 10000A；
- Sodium cell is central symmetry and the distribution of the electric field is completely symmetrical.

For the reasons above, this paper chose one quarter of sodium cell for three- dimensional simulation. As shown in Fig.2,it is a simplified model .

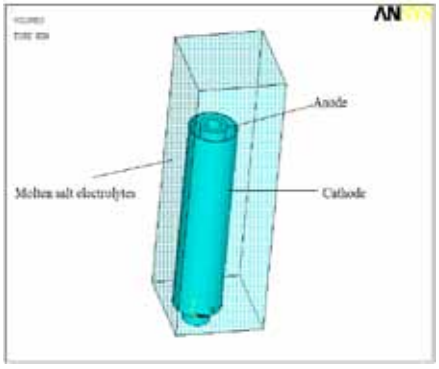


Fig. 2. Simplified physical model

2.2 Mathematical equations

The current fluctuations with time and phenomenon of current transmission lag in the electrolytic tank for the normal operation of the electrolytic tank can be ignored. Therefore, current field belongs to static electric field over the process of electrolysis. Based on the assessment principle, the calculation of the electric field pertaining to anode-cathode and molten salts in the Sodium electrolytic cells accords with the Laplace equation[5]:

$$\nabla^2 \phi = 0 \tag{1}$$

Equation (1) can be expressed by:

$$\frac{\partial}{\partial x}[\frac{1}{\rho_x}\frac{\partial \phi}{\partial x}]+\frac{\partial}{\partial y}[\frac{1}{\rho_y}\frac{\partial \phi}{\partial y}]+\frac{\partial}{\partial z}[\frac{1}{\rho_z}\frac{\partial \phi}{\partial z}]=0 \tag{2}$$

$$\Sigma \phi = \Sigma IR \tag{3}$$

Where ϕ is scalar voltage potential, I the total current and R the resistance of electrolyte.

Appling the finite difference method to equation (2), the potential value of the node can be obtained and then the intensity of electric field between nodes can be solved by using the relationships between electric field strength and potential:

$$\begin{aligned} E_x &= -\frac{\partial \phi}{\partial x} \\ E_y &= -\frac{\partial \phi}{\partial y} \\ E_z &= -\frac{\partial \phi}{\partial z} \end{aligned} \tag{4}$$

Ignoring the influence of the flow and non-electrostatic force to the electric charge, this is simply given by the expression:

$$J = \sigma E \tag{5}$$

Where ρ_x, ρ_y, ρ_z is the three-directional resistivity of the material that is changed with temperatures, σ is the conductivity of melt, E is the electric-field intensity and J is the current density.

The boundary conditions of the electric field can be determined by the selected unit types in the calculating process of the electric field:

- The voltage of cathode as foundation potential is 0V;
- Coupling voltage freedom on anode and stipulating that electric current is 10000A

2.3 Calculations of voltage of electrolyzer

The electrobath voltage includes three parts:

- Actual decomposition voltage

The actual decomposition voltage of electrolyte can be calculated by the theoretical decomposition voltage. According to the document, the theoretical decomposition voltage of sodium chloride under the standard condition is 2.19V [6]. Actually, the existence of ion concentration of reactants makes electrolysis overvoltage that dues to the effect of electrode polarization and thereby the actual decomposition voltage is different from theory decomposition voltage, the calculation of the actual decomposition voltage of ternary system whose temperature is kept for 660℃ used the following methods:

Converting the solubility of sodium chloride into molar concentration:

$$C = \frac{\frac{0.3}{58.5}}{\frac{0.2}{111} + \frac{0.5}{208} + \frac{0.3}{58.5}} = 0.5494\,(Mol/L) \tag{6}$$

The concentration of Na^+ touched to reaction interface of cathode:

$$C_{Na^+} = 1 \times C \times 30\% = 0.16482\,(Mol/L) \tag{7}$$

Identically, the concentration of Cl^- touched to reaction interface of anode:

$$C_{Cl^-} = 1 \times C \times 30\% = 0.16482\,(Mol/L) \tag{8}$$

The actual decomposition voltage of $NaCl$ can be obtained by the electrolysis principle:

$$E = E^0 - \frac{RT}{nF} ln\left(C_{Na^-} \times C_{Cl^-}\right) = 1.223 - \frac{8.314 \times 1303}{6 \times 96487} ln(0.16482 + 0.16482) = 2.29(V) \tag{9}$$

Where E^0 is the theory decomposition voltage under the standard state, R is molar gas constant, 8.314 $J/(mol \cdot K)$, T is the temperature, n is the number of electron gain or loss and F is faraday constant, 96500C/Mol.

- Structural voltage

Conductor materials that contact with electrolytic tank have resistance and the voltage drop caused by electricity flows through these materials that is connecting devices of the cell. In addition, current through the conductor into the cell that needs to pass through the anode and cathode which also have resistance that will cause the voltage loss in the same way.. As mentioned above, these form the drop of the structure voltage. The value of structure voltage of the sodium electrolysis cell which is given in references[7] is used in this paper.

- Melt voltage

The electrolyte solution with high temperature in the cell has resistance and when the current flows through the electrolyte solution， it would transform into voltage loss that be categorized as melt voltage drop． However it mainly converts the electric energy to heat energy continuously over the whole process to maintain the required temperature during the electrochemical reaction .This paper mainly studied the regularity of distribution of the melt voltage drop when the groove of the cell was changed.

3. Results and analysis

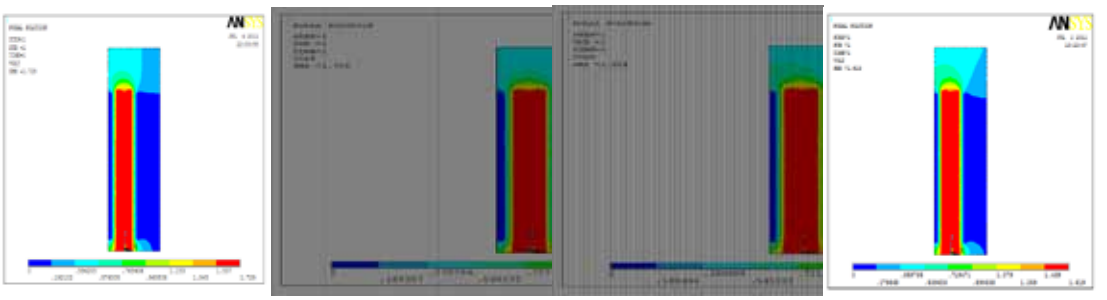


Fig. 3 (a) Isopotential in cell without aperture on anticathode; (b) Isopotential in cell with aperture on anode; (c) Isopotential in cell with aperture on cathode; (d) Isopotential in cell with aperture on anticathode

Fig.3 shows whether there are apertures on anticathode or not, the potential on the cathode and anode regarded as equipotential is substantially equal. The current field was divided into anodic and cathodic areas where the potential changes rapidly and the potential gradient is larger. This confirms electrolysis occurs mainly between the areas.

The different aperture locations affect little on the distribution of voltage. Considering the influence of the current density on the current efficiency, the cathode with aperture can increase the cathodic current density and accelerate metal precipitation rate, While flow field exists in the electrolytic tank, the hole on the cathode will make the precipitated melt owing to the increasing mobility of molten salt be brought back to molten salt electrolyte, which debase the current efficiency of electrolysis. So in order to strengthen liquidity, consider the situation with aperture on anode.

The melt voltage in cell with aperture on anticathode is greater than the melt voltage without aperture on anticathode, anode or cathode. Furthermore, the voltage with aperture on anode is closer to the voltage without aperture. On the basis of the adjustment of process parameters on the cell voltage of cell, this paper have to configure the situation with aperture on anode and the voltage is the best at the same time. The voltage of electrolyzer(6.814v) is composed by the actual decomposition voltage(2.29v), structure voltage(2.9v) and melt voltage(1.624v).

Fig.4 shows isopotential line is the most intensive nearby positive column where the electric potential gradient is maximum while isopotential line is more intensive round cathode. What causes this phenomenon is that the potential difference between cathode and slurry trench is far less than it between cathode and anode.

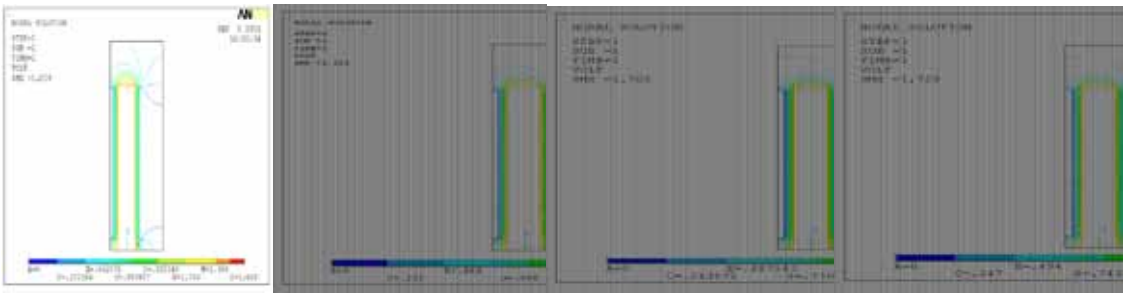


Fig. 4. (a) Isopotential lines in cell without aperture on anticathode; (b) Isopotential lines in cell with aperture on anode; (c) Isopotential lines in cell with aperture on cathode; (d) Isopotential lines in cell with aperture on anticathode.

The isopotential line of anticathode without aperture is vitally similar to them of anode with aperture, and their distributions on anode with aperture are similar to them on anticathode with aperture. Comparing the two cases above, the isopotential line of the upper part of anode in the later case relative to the former extend gradually to the top, and they are more intensive, which increases the voltage difference near the top. The presence of voltage difference will generate a lot of heat. According to Charles's law, the heat will enhance the gas pressure and reduce the velocity of the gas that is not easy for gas to discharge. This part of gas may make the precipitated metal be back into the electrolyte again, and then eliminate the current efficiency of electrolysis.

4. Conclusions

Three-dimensional mathematical model for one quarter groove of 40KA sodium cell was established, based on the feature of its structure, main conclusions are obtained as follows:

- The effect of different anticathode aperture location on the distribution of voltage of electrolysis cell was negligible. Taking account of that the cathode-anode current density influence the current efficiency and the change of groove type effect on the flow of electrolyte, so this paper only considered the situation with aperture on anode.
- The melt voltage in the cell with aperture is greater than the melt voltage without aperture on anticathode. According to the theoretical analysis and actual conditions, voltage in the cell with aperture on anode is natrium electrolytic working voltage, calculated as 6.814V.
- Compared to isopotential line with aperture on cathode and without aperture on anticathode, the isopotential line with aperture only on anode extend to the top and become more compact, which increases the voltage difference near the upper part of anode. The presence of voltage difference will generate great heat which will enhance the gas pressure and reduce the velocity of the gas that is not easy for gas to discharge. This part of gas may make the precipitated metal be back into the electrolyte again and eliminate the current efficiency of electrolysis. Therefore, the scheme that apertures are drilled only on anode is employed..

References

[1]Wu YF, Liu ZX, Ren YF, Li HS. Analog Simulation of the electric field in highly effective energy sodium electric tank with four anodes.Journal of In Mongolia University of Science and Technology;2008;27(1):90-93

[2]Wu YF, Li HS, Lang JL, Liu ZX. Numerical Simulation of Electric Field in Sodium Electrolytic Cell..Nonferrous Metals(Extractive Metallurgy);2011(11);28-31

[3]Dupuis M, Tabsh I. Thermo-electric coupled field analysis of aluminum reduction cell using ANSYS. Fifth International Conference and Exhibition. Pennsylvania: Pittsburgh;1991;20-24

[4]Bai FY. Production of sodium by Molten Salt Electrolysis. Sea-Lake-Salt and Chemical Industry;1996;25(1):22-27

[5]Richad D,Goulet P, Dupuis M, Fafard M. Thermo-chemo-mechanical modeling of a HALL-HÉROULT cell thermal bake-out. TMS Light Metals;2006;669-674

[6]Zhao GR. Application of high current density, natural circulation, bipolar-type ion-exchange membrane electrolyzers.Chlor-Alkali Industry;2007; (11):11-18

[7]Ren YH,Wang JB,He YD,Liu ZX. Calculation of electric field and analysis on body voltage in rare earth electrolysis cell. Journal of Baotou University of Iron and Steel Technology;2003;22(4):313-317